Inorganic spacers and their prospects for electrochemical nanotechnology

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Well-defined molecular spacers for electrified interfaces attract active attention in connection with the basic studies of long-range electron transfer and also with advanced nanotechnologies. The search for new systems of this sort is stimulated also by molecular electronics. Organic SH-derivatized compounds, despite their excellent properties, can hardly be used widely.

Recently we have demonstrated very attractive barrier properties of various tungstate and polytungstates adsorbed on mercury electrode [1]. The advantages of these spacers are already estimated by electrochemists and applied to various problems [2-4]. However, the fundamental features of oxometalate layers on metals are far from being clarified which induces many uncertainties in interpretation of experimental data and prognosing of nanotechnological modes.

The most important questions to be clarified are as follows:

- are the oxometalate layers continuous;
- what is their real thickness;
- does the nature of any species in solution affect the properties of layers;
- what time do we need to form equilibrium oxometalate layers on metals;
- what is the structure of the reaction layer on electrodes modified by oxometalates?

We present the results obtained in connection with the problems listed above on model mercury electrodes by means of electrocapillary measurements, classical polarography, chronoamperometry, and cyclic voltammetry. Some comparative data for gold and platinum electrodes are also reported.

Data of tungstate and polytungstate effects on various types of reactions (organic, complex and inorganic reactants) is compared with taking into account quantitatively the equilibrium and non-equilibrium surface coverages. The effects of competitive adsorption of tungstates and anionic reactants are found for a number of reactants, namely, peroxodisulfate (Fig.1) and tetrachloroplatinite (Fig.2). Time-dependent degree of inhibition is interpreted. The contributions of long-distance discharge via barrier layer and short-distance electron transfer are separated, and the potential region is found which correspond to the existence of exactly continuous layers.

The prospects of layer-by-layer deposition of metals with nm resolution in the presence of tungstates are formulated in the conclusion, being most important for nanotechnological applications.

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References

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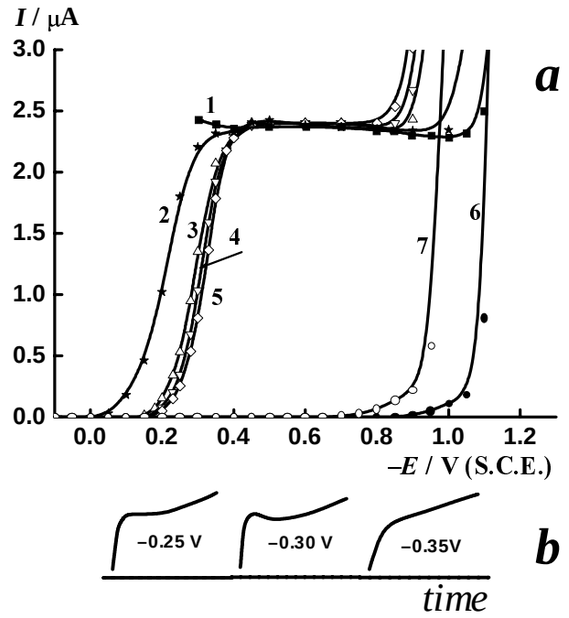

Fig.1. *a* - Polarograms measured on a dropping mercury electrode in 0.5 M acetic buffer (pH 4.7) in the presence of: (*1*) 10^{-3} N $K_2S_2O_8$ and with additions of (*2*) $5\cdot10^{-3}$ M Na_2WO_4 and (*3-5*) *x*M $Na_{10}[H_2W_{12}O_{42}]$ (*x*: (*3*) $2\cdot10^{-4}$, (*4*) $5\cdot10^{-4}$, (*5*) 10^{-3}); (6) $2\cdot10^{-4}$ M $Na_{10}[H_2W_{12}O_{42}]$ and (*7*) $5\cdot10^{-3}$ M Na_2WO_4; *b* – Current transients (normalized) measured at various potentials in 10^{-3} N $K_2S_2O_8$ + $5\cdot10^{-4}$ M $Na_{10}[H_2W_{12}O_{42}]$, drop life time is ca. 15 s.

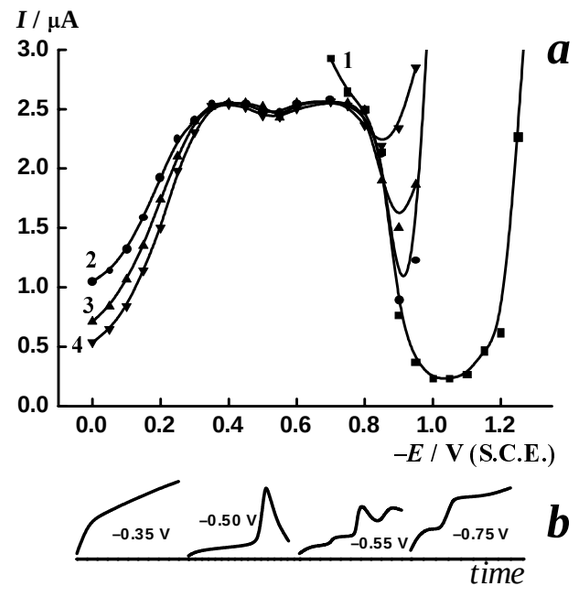

Fig.2. *a* - Polarograms measured on a dropping mercury electrode in 0.5 M acetate buffer (pH 4.7) in the presence of: (*1*) $5\cdot10^{-4}$ M K_2PtCl_4 with additions of (*2-4*) *x*M $Na_{10}[H_2W_{12}O_{42}]$ (*x*: (2) $2\cdot10^{-4}$, (3) $5\cdot10^{-4}$, (4) 10^{-3}); *b* - Current transients (normalized) measured at various potentials in $5\cdot10^{-4}$ M K_2PtCl_4 + $5\cdot10^{-4}$ M $Na_{10}[H_2W_{12}O_{42}]$, drop life time is ca. 15 s.